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(54) Abstract Title

**Glycol derivatives and blends thereof as gas hydrate inhibitors**

(57) A drilling, drill-in or completion fluid has water as a continuous phase and includes a blend of an ethylene glycol derivative and a propylene glycol derivative where the propylene glycol derivative is at least 10 vol % of the blend. The blend has the effect of suppressing gas hydrate formation and the propylene glycol derivative may be tripropylene glycol bottoms.

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Figure 1

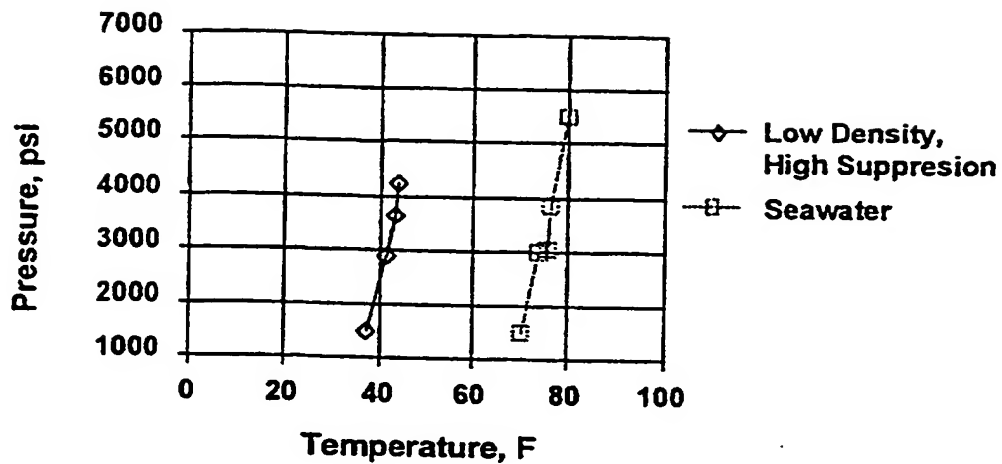


Figure 2

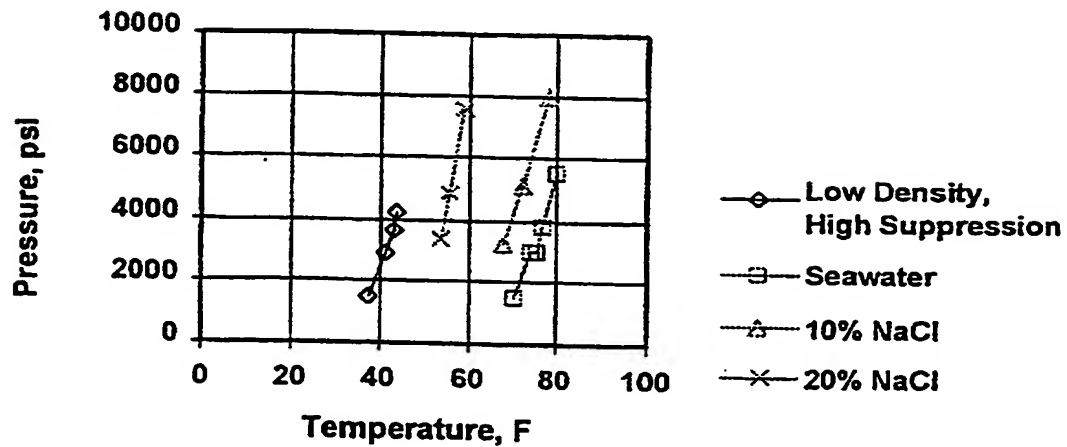
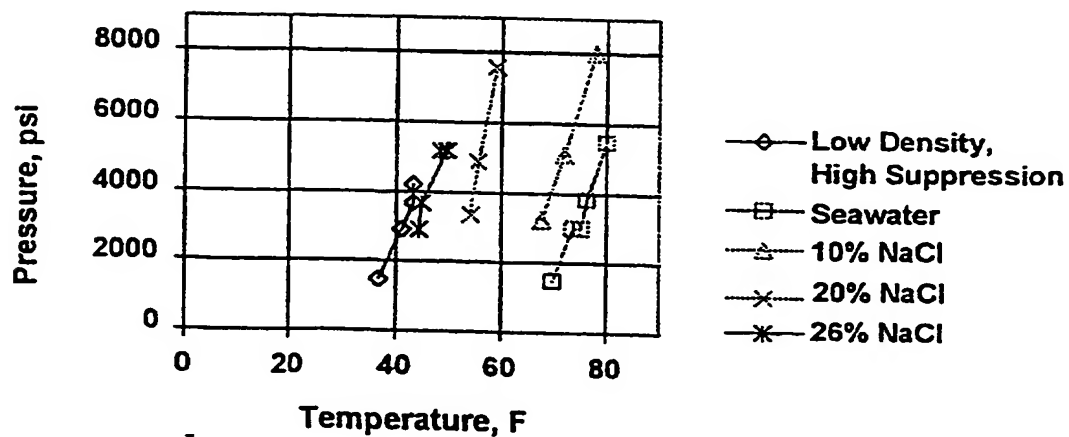


Figure 3



**TITLE: GLYCOL DERIVATIVES AND BLENDS THEREOF AS  
GAS HYDRATE INHIBITORS IN WATER BASE  
DRILLING, DRILL-IN, AND COMPLETION FLUIDS**

5 **Field of the Invention**

The present invention relates to methods and compositions for suppressing gas hydrate formation, for decreasing density, and for suppressing shale hydration in or by water-base drilling, drill-in, and completion fluids.

**Background of the Invention**

10 The petroleum industry continues to expand deepwater exploration and drilling efforts in many areas of the world. As drilling water depth increases, the potential for natural gas hydrate formation during drilling operations also increases.

Gas hydrates are solid, ice-like crystals that form under elevated pressures and at moderately low temperatures. Gas hydrates consist of water molecules which form  
15 five (pentagon) and six (hexagon) membered polygonal structures which combine to form closed structures (often called a "cage"). These "cages" totally enclose or trap a gas molecule. At high pressures, multiple "cages" tend to combine to form larger cages enclosing gas molecules. The resulting large crystalline assemblies are thermodynamically favored at elevated pressures. Under sufficient pressure, gas  
20 hydrates will form at temperatures well above the freezing point of water.

Primary promoters of gas hydrates are gas with "free" water present at or below its water dew point, low temperatures, and high pressures. Secondary promoters are high velocities, pressure pulsations, any type of agitation, and the

introduction of a small crystal of a hydrate. During deepwater drilling operations, all of the primary gas hydrate promoters are present.

The formation of gas hydrates in deepwater drilling operations creates safety concerns and can prevent proper operation of the blowout preventer during well-control operations, causing costly delays in controlling the wells. The use of a 20% sodium chloride/PHPA drilling mud system suppresses gas hydrate formation by 13.3-15.6°C (24-28°F) below that of freshwater. Often, however, it is necessary to suppress the temperature of hydrate formation even further—for example, during disconnects. “Spotting” of certain materials reportedly is effective to temporarily remove hydrates from various equipment and/or lines; however, spotting often is not performed until after gas hydrates have formed and caused the very delays sought to be avoided.

Another problem that occurs during deep water drilling is that “water-sensitive shales”—or formations having clay minerals as major constituents, such as shales, mudstones, siltstones, and claystones—often must be penetrated before reaching the hydrocarbon bearing zone. Various problems are encountered when drilling through water-sensitive shales, particularly using water-base drilling fluids. Water adsorption and hydration of the shale typically results in stress and/or volume increases, and can induce brittle or tensile failure of the formation. Such failures lead to sloughing, cave in, and stuck pipe. The volume increases also reduce the mechanical strength of the shales, and cause swelling of the wellbore, disintegration of cuttings in drilling fluid, and balling up of drilling tools.

Low density drilling fluids are needed which inherently will provide hydrate suppression under deep water drilling conditions, which will decrease water adsorption and hydration of water-sensitive shales; and which still have desirable rheology and fluid loss control properties for deepwater environments.

5 **Summary of the Invention**

The present invention provides a method for suppressing the formation of hydrates during drilling operations in a fluid comprising water as a continuous phase, the fluid being selected from the group consisting of a drilling, a drill-in, and a completion fluid having effective rheology and fluid loss control properties. The  
10 method comprises using as an integral component a hydrate suppressing amount of a non-toxic water-soluble organic compound selected from the group consisting of a monomer having a molecular weight up to about 800 and a polymer having a molecular weight up to about 2000.

**Brief Description of the Drawings**

15 **Figure 1 is a graph which illustrates the hydrate equilibrium points at a certain temperature and pressure for various water based drilling fluid formulations.**

**Figure 2 is a chart comparing hydrate phase equilibrium in a high hydrate suppression fluid containing ethylene glycol with seawater, 10% NaCl, and 20% NaCl.**

20 **Figure 3 is a chart comparing hydrate phase equilibrium in a low density, high hydrate suppression fluid containing ethylene glycol with seawater, 10% NaCl, and 20% NaCl, and 26% NaCl.**

### **Detailed Description of the Invention**

Gas hydrate suppression is needed for several types of fluids used during drilling operations. Drilling operations typically involve mounting a drill bit on the lower end of a drill pipe or "drill stem" and rotating the drill bit against the bottom of a hole to penetrate a formation, creating a borehole. A drilling mud may be circulated down through the drill pipe, out the drill bit, and back up to the surface through the annulus between the drill pipe and the borehole wall. The drilling fluid has a number of purposes, including cooling and lubricating the bit, carrying the cuttings from the hole to the surface, and exerting a hydrostatic pressure against the borehole wall to prevent the flow of fluids from the surrounding formation into the borehole.

A drilling fluid with a relatively high viscosity at high shear rates can place undesirable mechanical constraints on the drilling equipment and may even damage the reservoir. Higher viscosity fluids also exert higher pressures outward on the borehole, which may cause mechanical damage to the formation and reduce the ability of the well to produce oil or gas. Higher viscosity fluids also may fracture the formation, requiring a drilling shut down in order to seal the fracture. In deepwater environments, drilling muds must clean large, often deviated well bores, stabilize tectonically weak formations, inhibit mud making shales, and gain environmental acceptance.

A different fluid, known as a "drill-in" fluid, is pumped through the drill pipe while drilling through the "payzone," or the producing zone. A "completion fluid" is pumped down a well after drilling operations are complete, during the "completion phase," to remove drilling mud from the well and to support the well while the

equipment required to produce fluids to the surface is installed in the well. Each of these fluids needs a component that will suppress hydrate formation without adversely affecting the rheological and fluid loss control properties of the fluid.

A desirable characteristic of a drilling fluid in most applications is high density combined with an ability to flow easily at high velocities. In rheological terms, the drilling fluid typically should have a density of between about 0.9-2.5 g/cm<sup>3</sup>, and a relatively low plastic viscosity, preferably less than about 50, more preferably less than about 40, and most preferably less than about 30. Another desirable rheological property is yield point, which should be at least about 24.4 kg/100 m<sup>2</sup> (5 lb/100 ft<sup>2</sup>), preferably from about 24.4 to 146.4 kg/100 m<sup>2</sup> (5 to 30 lb/100 ft<sup>2</sup>).

In certain applications, lower density fluids are required in order to avoid fracturing the formation. A primary low density application is deep water drilling. As used herein, the term "deepwater drilling" is defined to mean drilling at water depths of greater than about 304.8 meters (1000 feet). The fluids used during deep water drilling preferably should have a density which is less than the fracture gradient of the formation being drilled through.

The present invention provides drilling fluids which incorporate as integral components hydrate inhibitors that are non-toxic, economical, and effective to inhibit hydrate formation in the fluid during drilling, drill-in, and completion operations without adversely affecting the rheological and/or fluid loss control properties of the fluid. The hydrate suppressors of the present invention are "low molecular weight water soluble organic compounds." "Low molecular weight" is defined to mean

nonpolymeric molecules having a molecular weight up to about 800, and a polymeric materials having a molecular weight up to about 2000, preferably those having a total molecular weight of up to about 1000.

Without limiting the present invention to any particular theory or mechanism of action, the low molecular weight water soluble organic molecules are believed to associate with the water molecules in the fluid and to interfere with either the availability of the water molecules or the ability of the water molecules to form polygonal water "cages." The result is that the temperature at which hydrates form is suppressed by at least about 10°F (5.56°C), preferably by at least about 30°F (16.7°C), most preferably by at least about 35°F (19.4°C). The hydrate suppressors suppress the formation of hydrates in a pressure and temperature range between about 3.45 MPa (500 psia) at 1.67°C (35°F) or lower to about 55.15 MPa (8000 psia) at 26.67°C (80°F) or lower, particularly between about 6.895 MPa (1000 psia) at 1.67°C (35°F) or lower to about 41.37 MPa (6000 psia) at 26.67°C (80°F) or lower.

Suitable hydrate suppressors for use in the invention include, but are not necessarily limited to glycols, polyglycols, polyalkyleneoxides, alkyleneoxide copolymers, alkylene glycol ethers, polyalkyleneoxide glycol ethers, carbohydrates, amino acids, amino sulfonates, alcohols comprising between about 1-3 carbon atoms, salts of any of the foregoing compounds, and combinations of the foregoing compounds.

Examples of suitable glycols and polyglycols include, but are not necessarily limited to ethylene glycols, diethylene glycols, triethylene glycols, tetraethylene glycols,



propylene glycols, dipropylene glycols, tripropylene glycols, and tetrapropylene glycols. Examples of suitable polyalkyleneoxides and copolymers thereof include, but are not necessarily limited to polyethylene oxides, polypropylene oxides, and copolymers of polyethylene oxides and polypropylene oxides. Suitable polyalkyleneoxide glycol ethers include, but are not necessarily limited to polyethylene glycol ethers, polypropylene glycol ethers, polyethylene oxide glycol ethers, polypropylene oxide glycol ethers, and polyethylene oxide/polypropylene oxide glycol ethers. Suitable carbohydrates include, but are not necessarily limited to saccharides and their derivatives. Suitable saccharides include, but are not necessarily limited to monosaccharides, such as fructose and glucose, disaccharides, and any polysaccharides having a molecular weight less than about 800. Suitable saccharide derivatives include, but are not necessarily limited to methylglucosides, methylglucamines, and the like. Suitable alcohols include, but are not necessarily limited to methanol, ethanol, propanol, and isopropanol.

One preferred hydrate suppressor is ethylene glycol. Surprisingly, ethylene glycol meets the current EPA requirements for discharge into U.S. waters.

A preferred embodiment of the hydrate suppressors of the present invention for use in deepwater drilling are blends comprising two components--an "ethylene glycol derivative" and a "propylene glycol derivative." In a preferred embodiment, the blend comprises at least about 10 vol% propylene glycol derivative, more preferably at least about 20 vol% propylene glycol derivative, and most preferably about 30 vol% propylene glycol derivative. The blend may comprise up to about 50 vol% propylene

glycol derivative or more.

Suitable ethylene glycol derivatives for use in the blend include, but are not necessarily limited to ethylene glycol, polyethylene glycols, and ethylene glycol ethers.

A preferred ethylene glycol derivative is ethylene glycol. Suitable propylene glycol derivatives for use in the blend include, but are not necessarily limited to propylene glycol, polypropylene glycols, and polypropylene glycol ethers. A preferred propylene glycol derivative for use in this preferred blend is tripropylene glycol bottoms (TPGB) obtained from Dow USA. TPGB comprises 5-20 wt% tripropylene glycol (CAS # 001638-16-0) with a balance of polypropylene glycol highers (CAS #025322-69-4).

10 Dow USA TPGB has the following physical properties:

Boiling point:	268°C (515°F)
Vapor pressure:	<0.01 mm Hg @ 20°C
Vapor density:	>1
Solubility in water:	Miscible
Specific Gravity:	1.023
Appearance:	Dark brown, viscous liquid
Odor:	Slight characteristic odor.
Flash point:	>140°C (285°F)

15 20 The specific gravity of TPGB -- under 1.05 -- is significantly lower than the specific gravity of ethylene glycol at 1.115.

The preferred blends of the present invention not only provide gas hydrate inhibition, the blends also provide improved shale inhibition compared to the use of ethylene glycol, alone, as a gas hydrate inhibitor. The organic molecules in the blend are believed to act as a semi-permeable barrier that separates the water molecules in the fluid from the shales, thus preventing water adsorption and hydration of the shale. The blends also can be formulated at lower densities than fluids which use salts for

hydrate suppression, and thus can reduce the risk of fracturing the formation during deep water drilling.

The preferred blend formulation of the present invention not only suppresses hydrate formation and water adsorption and hydration of water-sensitive shales, but also improves the overall performance of the water base drilling fluid by reducing the density of the fluid when compared to state of the art fluids which exhibit comparable hydrate suppression. Ethylene glycol and a preferred formula of the preferred ethylene glycol/TPGB blend also have been found to meet the current EPA requirements for discharge into U.S. waters.

As used herein, the term "non-toxic" is defined to mean that a material meets the applicable EPA requirements for discharge into U.S. waters. Currently, a drilling fluid must have an  $LC_{50}$  (lethal concentration where 50% of the organisms are killed) of 30,000 parts per million (ppm) suspended particulate phase (SPP) or higher to meet the EPA standards. The mysid shrimp toxicity test for ethylene glycol resulted in an  $LC_{50}$  of 970,000 ppm SPP—over 30 times the minimum EPA standard for discharge into coastal waters. The mysid shrimp toxicity test for a preferred ethylene glycol/TPGB blend (65 wt%/35 wt%, respectively) resulted in an  $LC_{50}$  of 200,000 ppm of the SPP—over 6 times the minimum EPA standard for discharge into coastal waters. Ethylene glycol and the preferred blend have the added advantage that they produce no sheen on the receiving waters.

Substantially any water based drilling, drill-in, or completion fluid may be treated according to the present invention. An example formulation of one barrel of a

preferred low density deepwater drilling fluid containing ethylene glycol as a hydrate suppressor is shown in the following Table:

Product	Concentration
Fresh Water	0.66 bbl
MIL-GEL	15 lb/bbl
NaOH	0.1 lb/bbl
MIL-PAC LV	1.0 lb/bbl
BIO-LOSE	1.0 lb/bbl
Sodium Chloride	38.4 lb/bbl
ethylene glycol	0.30 bbl
<i>Total = 1 bbl</i>	

- MIL-GEL, MIL-PAC, and BIO-LOSE are products which may be obtained from Baker Hughes Inteq, Houston, Texas. The other listed materials are commodities which are commercially available from numerous sources well known to persons of ordinary skill in the art.

- An example formulation of one barrel of a preferred low density deepwater drilling fluid containing a preferred ethylene glycol/TPGB blend is shown in the following Table:

Product	Concentration
Drillwater	0.8 bbl
NEW DRILL PLUS	0.75 ppb
NaCl	23% by wt
MIL-PAC LV	1 ppb
BIO-LOSE	2.5 ppb
XCD Polymer	0.75 ppb
65/35 ethylene glycol/TPGB	30% by wt
<i>Total = 1 bbl</i>	

NEW DRILL PLUS is a product which may be obtained from Baker Hughes INTEQ.

Houston, Texas. XCD Polymer is available from Kelco Rotary, San Diego, California.

TPGB is available from a number of suppliers, preferably Dow USA. The other listed materials are commodities which are commercially available from numerous sources well known to persons of ordinary skill in the art.

- 5        The fluid should contain at least about 5 vol% of the hydrate suppressing blend, preferably at least about 10 vol%, more preferably in the range of from about 10 to about 80 vol%, and most preferably in the range of from about 10 to about 30 vol% of the blend.

- 10       Fig. 1 is a graph illustrating the hydrate equilibrium points at a certain temperature and pressure for various water based drilling fluid formulations comprising salt vs. 10% of an ethylene glycol/TPGB blend. Every condition or point to the right of the lines is where a gas hydrate would not form while every condition or point to the left of these lines is where gas hydrates would form. The 23% NaCl fluid (containing 10% 65/35 blend of EG/TPGB) is the most inhibitive fluid in regard to gas hydrate inhibition with a hydrate suppression of approximately 23.34°C (42°F).
- 15

Fluid Type	Hydrate Suppression $\Delta T$ (°C/°F)	Density, g/cm <sup>3</sup> (lb/gal)
Fresh Water	0	1 (8.33)
Sea Water	2.22/ 4	1.02 (8.5)
10% NaCl	7.78/14	1.08 (9.0)
20% NaCl	16.11/29	1.15 (9.6)
23% NaCl	17.22/33	1.17 (9.8)
23% NaCl/ 10% 65/35 blend EG/TPGB	23.34/42	1.15 (9.6)

Persons of ordinary skill in the art will be able to use the low molecular weight water soluble organic compounds to achieve a desired level of gas hydrate suppression at given conditions of temperature and pressure.

Because of their relatively low density, fluids containing a blend of ethylene glycol derivative and propylene glycol derivative should prove useful when  
5 encountering gradients having poor fracture integrity. The density of the fluid can be reduced by reducing the salt content of the fluid. In fact, it may be possible to eliminate the need for any salt to suppress hydrate formation, and to decrease water adsorption and hydration of water-sensitive shales. Even with a lowered salt content,  
10 the temperature of hydrate formation should be reduced by approximately 5°C (9°F) when the fluid contains at least about 10 vol% of the EG/TPGB blend.

The invention will be more clearly understood with reference to the following examples, which are illustrative only and should not be construed as limiting the invention. In the following Examples, gas hydrate formation was simulated using a gas  
15 hydrate generator developed by Milpark Drilling Fluids (now Baker Hughes INTEQ). The gas hydrate generator consisted of a high-pressure (11,000-psi [76,834 kPa]) vessel, temperature and pressure capabilities, and an IBM PC for control of the system and data acquisition. To begin a gas hydrate test, mud was placed into the autoclave cell, the cell was capped and a vacuum was pulled on the cell for 15 minutes while  
20 stirring at 500 rpms to remove the air from the cell. After evacuation of the cell, the cell was pressurized with a simulated Green Canyon natural gas having the following mole% composition: 87.243% methane; 0.403% nitrogen; 7.57% ethane; 3.08%

propane; 0.51% isobutane; 0.7% normal butane; 0.202% isopentane; and 0.20% normal pentane.

A cooling bath was raised to cover the cell, and the cell was allowed to reach an equilibrium temperature then cooled at a rate of 5°F (2.8°C) per hour until hydrate  
5 formation was detected. To detect hydrate formation, the computer monitored the temperature (cell and bath) and applied pressure. When the slope of the pressure verses temperature curve changed significantly, hydrates were starting to form (one volume of hydrates can contain 170 volumes of gas at standard conditions).

Once hydrates started forming, the bath temperature was held constant for  
10 about 10 hours to allow maximum hydrate formation before heating the bath to room temperature (1.5°F/hour [0.83°C/hour]). During heatup, the gas hydrates became less stable, resulting in the gas being released from the hydrate structure, and pressure  
increasing. When all of the gas was released, the pressure returned to the initial pressure recorded from the cool-down cycle. This is known as the dissociation point--  
15 that is, no hydrates are present at this pressure and temperature.

### EXAMPLE I

Drilling fluids having the same composition except for the base fluid were subjected to hydrate equilibrium testing. The base fluid was varied as follows: 10% NaCl/30% by volume ethylene glycol; sea water; 10% NaCl; 20% NaCl; and, 26%  
20 NaCl.

Each run generated the pressure-temperature results shown in the following table, which is depicted in chart form in correspondingly numbered Figures (1, 2, and 3).

Component	Ethylene Glycol/10% NaCl	Seawater	10% NaCl	20% NaCl	26% NaCl
Drill Water, bbls			0.44	0.43	0.425
Seawater, bbls		1	0.44	0.43	0.425
Tap Water, bbls	0.66				
MIL-PAC LV, lbs/bbl	1		1.5	1.5	1.5
BIO-LOSE, lb/bbl	1		3	3	3
Caustic Soda, lb/bbl	0.1		1.25	1.25	1.25
Drilled solids, lb/bbl			20	20	20
Ethylene glycol, bbls	0.3				
NaCl, lb/bbl	34		34	76	104
NEW DRILL HP, lb/bbl	0.5		1.5	1.5	1.5
MIL-GEL, lb/bbl	15		10	10	10
MIL-BAR, lb/bbl			68	33	9
XCD Polymer, lb/bbl			0.08	0.25	0.75
Density, ppg	9.4		10.5	10.5	10.5
Rheology @ 120°F					



Component	Ethylene Glycol/10% NaCl	Seawater	10% NaCl	20% NaCl	26% NaCl
P.V., cPs	11		19	18	18
Y.P., lb/100ft <sup>2</sup>	10		12	11	14
Gels, lb/100ft <sup>2</sup>	7/14		3/17/23	8/14/19	6/11/18
API, cc's/30 min	4		4	4.6	4.2
pH	7.4		9.45	9.45	9.5

MIL-GEL, MIL-PAC, MIL-BAR, NEW DRILL HP, and BIO-LOSE are products which may be obtained from Baker Hughes Inteq, Houston, Texas. XCD Polymer was obtained from Kelco Rotary, San Diego, California.

The ethylene glycol fluid imparted greater hydrate suppression than even the saturated sodium chloride fluid. The saturated sodium chloride fluid had a density of 10.0 lbs/gal; therefore, the ethylene glycol imparted greater gas hydrate suppression with an approximate 1.0 lbs/gal density advantage.

#### EXAMPLE 2

The fluid containing ethylene glycol from Example 1 was subjected to increasing doses of low gravity solids to determine the effect on the fluid properties. API RP 10B and 13B were used to determine the specifics for the various drilling fluids, and the resulting effects on rheological properties, and fluid loss.

Initial/hot roll	Hot Rolled	Initially	Hot Rolled	Initially	Hot Rolled	Initially	Hot Rolled
Aging Temperature	150		150		150		150
Aging Hours	16		16		16		16
Tapwater, bbls	0.66	0.66	0.66	0.66	0.66	0.66	0.66

Mil-Pac LV, lbs/bbl	1	1	1	1	1	1	1
Bio-Lose, lbs/bbl	1	1	1	1	1	1	1
Caustic, lbs/bbl	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Rev-Dust, lbs/bbl	-	9	9	45	45	63	63
ethylene glycol, bbls	.30	.30	.30	.30	.30	.30	.30
NaCl, % by wt.	10	10	10	10	10	10	10
New-Drill HP, lbs/bbl	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Mil-Gel, lbs/bbl	15	15	15	15	15	15	15
Density, ppg	9.42						
Rheologies @	120	120	120	120	120	120	120
600 rpm	32	38	42	42	37	43	53
300 rpm	21	26	28	29	24	28	37
200 rpm	18	21	24	24	20	24	30
100 rpm	14	16	18	18	15	18	23
6 rpm	9	10	11	12	8	11	13
3 rpm	8	9	9	11	7	10	12
Plastic Viscosity, cP	11	12	14	13	13	15	16
Yield Point, lbf/100	10	14	14	16	11	13	21
YZ Value	7	8	7	10	6	9	11
Initial Gel, lbf/100 ft <sup>2</sup> s	7	8	7	10	7	9	10
10 min Gel, lbf/100	14	25	20	31	16	30	23
API Fluid Loss, mls	4	4.2	3.6	4	3.8	4.2	4
pH	7.4	7.6	7.6	7.8	7.8	7.6	7.7
Lubricity Coefficient	0.19						

The fluid containing ethylene glycol had a relatively low density of 9.42 ppg, exhibited tolerance to low gravity solids contamination, and exhibited satisfactory rheological and fluid loss properties.

### EXAMPLE 3

Fluids having the following composition were made and API RP 10B and 13B were used to determine the specifics for the various drilling fluids, the resulting effects on rheological properties, and fluid loss.

Initial/Hot Roll Aging Temperature Aging Hours	Initially	Hot Rolled 150 16	Initially	Hot Rolled 150 16
Tarwater, bbls		0.66	0.66	0.66
Mil-Pac LV, lbs	1	1	1	1
Bio-Lose, lbs	1	1	1	1
Caustic, lbs	0.1	0.1	0.1	0.1
Cement, lbs	1.5	1.5	5	5
Rev-Dust, lbs	-	-	-	-
Ethylene glycol, bbls	.30	.30	.30	.30
NaCl, % by weight	10	10	10	10
New-Drill HP, lbs	0.5	0.5	0.5	0.5
Mil-Bar, lbs	-	-	-	-
Mil-Gel, lbs	15	15	15	15
Density, ppg				
Rheologies @	120	120	120	120
800 rpm	32	30	26	26
600 rpm	21	20	14	14
400 rpm	17	16	10	10
200 rpm	13	12	6	6
8 rpm	8	7	1	2
9 rpm	7	6	1	1
Plastic Viscosity, cP	11	10	12	12
Yield Point, lbf/100 ft <sup>2</sup>	10	10	2	2
YZ Value	6	5	1	0
Initial Gel, lbf/100 ft <sup>2</sup> s	6	6	1	1
10 min Gel, lbf/100 ft <sup>2</sup> s	17	14	1	1
API Fluid Loss, mls	4	4.2	4	4
pH	11.1	11.3	11.6	12.4

The fluids had a low density, exhibited low cement contamination, and exhibited satisfactory rheological and fluid loss properties.

5

#### EXAMPLE 4

Test wafers or pellets were prepared from a reactive Mississippi Canyon shale sample. XRD analysis indicated that the sample consisted of 40-45% mixed layers and

had a greater than 80% expandable matrix. The CEC of the sample was 18 meq/100 g.

Wafers were weighed and measured before being placed and hot rolled in a sample of a fluid having the compositions outlined below. The samples of fluid containing the pellet or wafer were hot rolled for approximately 48 hours in an oven at approximately 65°C (150°F). After hot rolling, the wafers were recovered. The percent recovery, hydration (water uptake), volume change, and hardness were determined for each wafer. With the exception of hardness, which is expressed as a direct measurement by durometer, the changes in each parameter were calculated by comparison to the initial values. The fluid samples included HF-100N, a polyglycerine material currently available from Baker Hughes INTEQ for gas hydrate suppression, ethylene glycol, and the indicated blends of ethylene glycol and TPGB obtained from Baker Hughes INTEQ. The results indicate higher recovery, higher hardness, lower hydration, and lower volume change—in other words, improved shale inhibition characteristics—using the blend of ethylene glycol with TPGB. The results also indicate that fluids made using the ethylene glycol/TPGB blend had a lower density than pure ethylene glycol.

The deepwater fluid formulation used was:

Drillwater	0.8 bbls
Biolose	2.5 ppb
Mil Pac IV	1 ppb
New Drill Plus	0.85 ppb
XCD Polymer	0.75 ppb
NaCl	23% by weight

The eight test fluids contained:

- 1) 23% NaCl/PHPA\*/30% HF 100 N;
- 2) 23% NaCl/PHPA/30% ethylene glycol;
- 3) 23% NaCl/PHPA/30% ethylene glycol/TPGB @ 90/10 blend;
- 4) 23% NaCl/PHPA/30% ethylene glycol/TPGB @ 80/20 blend;
- 5) 23% NaCl/PHPA/30% ethylene glycol/TPGB @ 65/35 blend;
- 6) 23% NaCl/PHPA/30% ethylene glycol/TPGB @ 65/35 blend;
- 7) 23% NaCl/PHPA/30% ethylene glycol/TPGB @ 60/40 blend;
- 8) 23% NaCl/PHPA/30% ethylene glycol/TPGB @ 50/50 blend.

\*PHPA refers to partially hydrolyzed polyacrylamide.

The yield point of all of the test fluids was maintained at 15 lb/100 square feet with small additions of XCD polymer. The pH of the fluids also was maintained at 7.0.

Each fluid was prepared by shearing in a Silverson blender for 45 minutes. The fluids were dynamic-aged 4 hours at  $65 \pm 0.5^\circ\text{C}$  ( $150 \pm 5^\circ\text{F}$ ) and stirred again for 5 minutes by a Prince Castle mixer. The fluids were stabilized for 16 hours at  $65 \pm 0.5^\circ\text{C}$  ( $150 \pm 5^\circ\text{F}$ ) and stirred again for 5 minutes on a Prince Castle mixer. The fluids containing shale wafers were then dynamically aged for 48 hours at  $65 \pm 0.5^\circ\text{C}$  ( $150 \pm 5^\circ\text{F}$ ) and the rheological properties ( $48.9^\circ\text{C}/120^\circ\text{F}$ , API, 100-psi differential) were measured.

The following were the properties of the test fluids after stabilizing:

FLUID	#1	#2	#3	#4	#5	#6	#7	#8
Density, lb/gal	10	9.7	9.68	9.66	9.65	9.64	9.63	9.62
600 Fann rpm	42	51	46	44	42	41	40	40

FLUID	#1	#2	#3	#4	#5	#6	#7	#8
300 Fann rpm	27	34	32	30	28	28	27	26
200 Fann rpm	20	22	21	20	21	21	20	19
100 Fann rpm	13	14	12	12	13	13	13	12
06 Fann rpm	3	3	3	3	3	3	3	3
03 Fann rpm	2	2	2	2	2	2	2	2
PV (cp@ 48.9°C/120°F)	15	17	14	14	14	13	13	14
YP kg/m <sup>2</sup> (lb/100 sq ft)	58.6 (12)	83 (17)	87.8 (18)	78.1 (16)	68.3 (14)	73.2 (15)	68.3 (14)	58.6 (12)
10 sec gel kg/m <sup>2</sup> (lb/100 sq ft)	14.6 (3)	19.5 (4)	19.5 (4)	19.5 (4)	14.6 (3)	14.6 (3)	14.6 (3)	14.6 (3)
10 min gel kg/m <sup>2</sup> (lb/100 sq ft)	19.5 (4)	24.4 (5)	24.4 (5)	24.4 (5)	19.5 (4)	19.5 (4)	9.8 (2)	9.8 (2)
API Filtrate (ml)	7.6	6.8	6.8	6.4	6.0	5.8	5.8	5.4

The resulting rheological values show a very mild depletion in the top end Fann 35 readings while improving API fluid loss values by providing a thinner more lubricious wallcake. The properties of the 65/35 blend #6 are very similar to the fluid made using HF 100N (#1) except for the improvement in API fluid loss.

#### EXAMPLE 5

The fluids prepared in Example 1 were subjected to the shale wafer test, which measures the disintegration properties of a particular shale in contact with a drilling fluid or liquid composition over a measured time period. Shale disintegration was measured and recorded in four ways:

-Weight recovery in weight percent

- Shale hydration in weight percent
- Change in shale wafer hardness (durometers)
- Increase or decrease in shale wafer volume (percent change from original size)

Shale cuttings which were heavily contaminated with water base mud were  
5 washed using a fine spray of water from a wash bottle, taking care to minimize loss of  
fine colloidal material. A 180 micron sieve was used for washing in order to retrieve  
as much of the solids as possible. The activity of the shale cuttings was measured and  
recorded, and the cuttings were air dried for about 24 hours on a soft absorbent tissue  
under laboratory conditions. The shale cuttings were dried in an oven at a temperature  
10 not exceeding about  $65^{\circ}\text{C} \pm 3^{\circ}\text{C}$  ( $150^{\circ}\text{F} \pm 5^{\circ}\text{F}$ ) for about  $4 \pm 1$  hour.

The cuttings then were ground using a grinding mill to pass through a 180  
micron screen. An amount of water was added based on an estimate of the connate  
water content. Each pressed wafer weighed about 20 g. Generally 8 to 15 percent by  
weight of water covered most of the interstitial water contents.

15 The appropriate amount of deionized water was added to a weighed amount of  
ground shale in a jar. The amount of water added was recorded. The jars were  
capped with a lid and shaken. To enhance the wetting process, the moist shale was  
placed in a blender and stirred for 15-30 seconds and worked to a homogenous semi-  
sticky paste. The mortar was scraped with a spatula to remove any adherent material.  
20 Samples comprising about  $20 \pm 1$  g of the semi-sticky shale were placed into stainless  
steel die, which were precoated with a light oil to aid in release of the wafer. A piston,  
which also was precoated with the light oil, and was inserted and the die was  
positioned onto the press plate holder. A pressure of  $41.32 \text{ MPa} \pm 1.47 \text{ MPa}$  ( $6000 \pm$

200 psig) was applied for about  $2 \pm 0.5$  minutes. The pressure then was released and the wafer removed from the die. One of the wafers was weighed ( $W_1$ ). The wafer then was dried in an oven at  $104 \pm 3^\circ\text{C}$  ( $220 \pm 5^\circ\text{F}$ ) to constant weight and the weight recorded ( $W_2$ ). From the weight difference, the percent moisture content was

5 calculated and applied to all wafers used in the series. The wafer used to determine this value was discarded.

Each wafer was weighed and calipered and the values recorded. Durometer tests were made in triplicate and the results recorded. Each jar was hot rolled for about 16 hours at about  $65^\circ\text{C}$  ( $150^\circ\text{F}$ ). The jars were removed from the oven and

10 cooled, and the fluid was poured over a 40 micron sieve to retrieve the wafer from the fluid. The wafers were carefully dried with a soft absorbent tissue, and immediately weighed ( $W_3$ ). The hardness (durometer) of the wafer was measured in triplicate. The wafers were calipered to obtain an average diameter and height, and then dried at  $66-104^\circ\text{C}$  ( $150-220^\circ\text{F}$ ) for about 16 hours and reweighed ( $W_4$ ).

15 The following nomenclature was used in making calculations (weight being in g):

$W_1$  = Weight of Pressed Wafer  
 $W_2$  = Weight of Pressed Wafer Dried to Constant Weight  
 $W_3$  = Weight of Wafer After Hot-Rolling 16 hr  
 $W_4$  = Weight of Wafer After Hot-Rolling 16 hr and drying to constant weight  
 $V_1$  = Volume of Pressed Wafer in  $\text{m}^3$   
 $V_2$  = Volume of Wafer After 16 hr Hot-Rolling in  $\text{m}^3$   
 $P_1$  = Average Durometer Dial Reading of Pressed Wafer  
 $P_2$  = Average Durometer Dial Reading of Wafer After 16 hr Hot-Rolling

20  
25

The following formulas were used to determine the parameters tabulated in the table below:



% Moisture in Pressed Shale Wafer (assuming all wafers in the test series had the same moisture):

$$\% \text{ Moisture} = 100 \times \frac{W_1 - W_2}{W_2}$$

$$\text{Shale Recovery, \% by weight} = 100 \times \frac{W_4}{W_2}$$

$$\text{Shale Hydration, \% by weight} = 100 \times \frac{W_4 \left( 1 + \frac{\% \text{ moisture}}{100} \right)}{W_4 \left( 1 + \frac{\% \text{ moisture}}{100} \right)}$$

$$\text{Volume Change of Shale Wafer, } m = \frac{V_1 - V_2}{V_1}$$

$$\% \text{ Change in Hardness} = 100 \times \frac{P_1 - P_2}{P_1}$$

The following table tabulates the results of the shale inhibition testing:

PARA-METER	#1	#2	#3	#4	#5	#6	#7	#8
Percent Moisture	10	10	10	10	10	10	10	10
Initial Wt, g	18.8	18.8	19.6	19.4	19.3	19.4	19.3	18.8
Final Wt, g	14.6	12.8	13.6	14.2	14.8	17.2	16.6	16.4
Wet Wt, g	17.8	16.6	17.2	17.6	18.2	19	18.8	18.2
Hydra-tion	10.8	17.9	15.0	12.7	11.8	0.4	3.0	0.9

PARA-METER	#1	#2	#3	#4	#5	#6	#7	#8
% Recovery	86.3	75.7	77.1	81.3	85.2	98.5	95.6	96.9
% Volume Change	4.0	17.3	14.2	12.0	8.8	5.3	6.6	8.8
Hardness	90	74	78	85	88	90	90	90
Remarks	Intact	Hydrated	Hydrated	Hydrated	Intact	Intact	Intact	Intact

A remarkable improvement was seen in the hardness values of the shale wafers as TPGB was incorporated with ethylene glycol. A 65/35 blend reached the same effectiveness as HF 100N with a 90 shale hardness value and outperformed HF 100N in the ability to keep the shale from hydrating. While extremely good inhibition results were found with the 60/40 and 50/50 blends, hardness values seem to have leveled off close to their initial values of 94.

#### EXAMPLE 6

Gas hydrate formation was simulated as in Examples 1-3. The fluid containing 23% NaCl/10% by volume of a 65/35 EG/TPGB blend produced a hydrate suppression of 23.34°C (42°F) compared to fresh water. A 26% NaCl fluid had a hydrate suppression of 19.45°C (35°F) while having a density of 1.2 g/cm<sup>3</sup> (10 lb/gal); therefore, the EG/TPGB blend imparted greater gas hydrate suppression with an approximate 0.048 g/cm<sup>2</sup> (0.4 lb/gal) density advantage.

#### EXAMPLE 7

Several deep water drilling formulations were tested for rheological and shale stability data using the procedures described in Examples 4 and 5, respectively. As

shown in the following table, the fluid containing the EG/TPGB blend gave superior shale stability as measured by shale hydration, hardness, and recovery after dynamic aging as compared to a standard formulation and a fluid containing another common gas hydrate shale inhibitor:

Parameter	Base Fluid	65/35 EG/TPGB	Product A
<b>Formulation:</b>			
Tapwater, bbl	0.8	0.8	0.8
MIL PAC LV, lb/kg (lb/bbl)	0.373 (1)	0.373 (1)	0.373 (1)
65/35 EG/TPGB, bbls	-	0.30	-
Product A, bbls	-	-	0.30
NaCl, % by wt	23	23	23
NEW-DRILL Plus, kg/bbl (lb/bbl)	0.28 (0.75)	0.28 (0.75)	0.28 (0.75)
XAN-PLEX D, kg/bbl (lb/bbl)	0.28 (0.75)	0.28 (0.75)	0.28 (0.75)
<b>Properties:</b>			
Density, g/cm <sup>3</sup> (ppg)	1.15 (9.6)	1.18 (9.85)	1.2 (10.0)
Rheology @ °C/°F	48.9/120	48.9/120	48.9/120
Plastic Viscosity, cP	16	13	15
Yield Point, kg/100m <sup>2</sup> (lb/100 ft <sup>2</sup> )	63.44 (13)	73.2 (15)	58.56 (12)
YZ Value	1	1	1
Initial Gel, kg/100m <sup>2</sup> (lb/100 ft <sup>2</sup> )	9.76 (2)	14.64 (3)	14.64 (3)

Parameter	Base Fluid	65/35 EG/IPGB	Product A
10 min. gel, kg/100m <sup>2</sup> (lb/100 ft <sup>2</sup> )	14.64 (3)	19.52 (4)	19.52 (4)
API Fluid Loss, ml	6.0	5.8	7.68
Shale Inhibition:			
Hardness Value	75	90	90
Recovery, %	74	98.5	86.3
Hydration, %	18	0.4	10.8

Persons of ordinary skill in the art will appreciate that many modifications may be made to the embodiments described herein without departing from the spirit of the present invention. Accordingly, the embodiments described herein are illustrative only and are not intended to limit the scope of the present invention.

Claims

- 5 1. A fluid comprising water as a continuous phase and  
being selected from the group consisting of a drilling,  
a drill-in, and a completion fluid, the continuous phase  
comprising a gas hydrate suppressing amount of a blend  
comprising a first amount of an ethylene glycol  
10 derivative at a ratio to a second amount of a propylene  
glycol derivative, wherein the second amount is at least  
about 10 vol% of the blend.
- 15 2. The fluid of claim 1 wherein the ratio is 65:35.
3. The fluid of claim 1 or 2 wherein the second amount  
is from about 10 vol% to about 50 vol% of the blend.
- 20 4. The fluid of any of claims 1 to 3 wherein the gas  
hydrate suppressing amount is from about 10 to 80 vol%  
of the fluid.
- 25 5. The fluid of any of claims 1 to 4 wherein the  
ethylene glycol derivative is ethylene glycol; and  
the propylene glycol derivative is tripropylene glycol  
bottoms.
- 30 6. An additive for a fluid selected from the group  
consisting of a drilling, a drill-in, and a completion  
fluid, the additive comprising a blend comprising a  
first amount of an ethylene glycol derivative at a ratio  
to a second amount of a propylene glycol derivative,  
wherein the second amount is from 10 vol% to 50 vol% of  
the blend.
- 35 7. The additive of claim 6 wherein said ethylene  
glycol derivative is ethylene glycol; and said propylene  
glycol derivative is tripropylene glycol bottoms.

**Amendments to the claims have been filed as follows**

1. A fluid comprising water as a continuous phase and being selected from the group consisting of a drilling, a drill-in, and a completion fluid, the continuous phase further comprising a gas hydrate suppressing amount of a blend comprising a first amount of an ethylene glycol derivative at a ratio to a second amount of a propylene glycol derivative, wherein the second amount is at least about 10 vol% of the blend.

2. The fluid of claim 1 wherein the ratio is 65:35.

3. The fluid of claim 1 or 2 wherein the second amount is from about 10 vol% to about 50 vol% of the blend.

4. The fluid of any of claims 1 to 3 wherein the gas hydrate suppressing amount is from about 10 to 80 vol% of the fluid.

5. The fluid of any of claims 1 to 4 wherein the ethylene glycol derivative is ethylene glycol; and the propylene glycol derivative is tripropylene glycol bottoms.

6. An additive for a fluid selected from the group consisting of a drilling, a drill-in, and a completion fluid, the additive comprising a blend comprising a first amount of an ethylene glycol derivative at a ratio to a second amount of a propylene glycol derivative, wherein the second amount is from 10 vol% to 50 vol% of the blend.

7. The additive of claim 6 wherein said ethylene glycol derivative is ethylene glycol; and said propylene glycol derivative is tripropylene glycol bottoms.



INVESTOR IN PEOPLE

Application No: GB 0122134.0  
Claims searched: 1-7

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Examiner: Dr. Lyndon Ellis  
Date of search: 4 October 2001

# **Patents Act 1977** **Search Report under Section 17**

## **Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): E1F FGP, FPE

Int Cl (Ed.7): E21B

Other: Online: EPODOC, WPI, JAPIO

## **Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0322736 A2 (Aqualon)	-
A	US 4830765 (Hughes)	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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